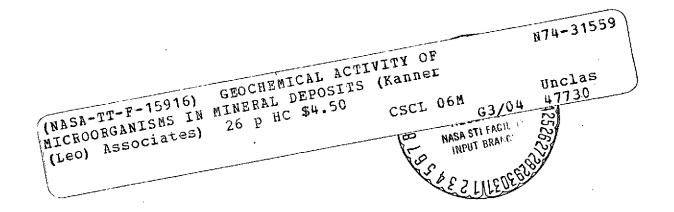
GEOCHEMICAL ACTIVITY OF MICROORGANISMS IN MINERAL DEPOSITS S. I. Kuznetsov

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16. Abstract The activity of microorganisms was investigated in deposits of oil, ozokerite, sulfur, sulfide ores, and nonferrous metals and in lakes where deposition of lake iron-manganese ore takes place. Data are presented on distribution and activity of individual groups of microorganisms. Diagrams illustrating participation of the microorganism in formation or destruction of mineral deposits were drawn on the basis of these experiments.						
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GEOCHEMICAL ACTIVITY OF MICROORGANISMS IN MINERAL DEPOSITS

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Until the 1930's, the roles of microorganisms in the circula- /301*
tion of matter in nature were given comparatively little attention. The initiator of the concept of the importance of microorganisms in geochemical processes undoubtedly was V. I.
Vernadskiy, and his formulation, expressed in Outlines of Geochemistry, coincides closely in time with the period of organization of the Institute of Microbiology, in the Academy of Sciences system. He wrote: "The foundations of our opinions on the "Universe," on "Nature," and on the "Single Whole," of which many spoke in the eighteenth century and the first half of the nineteenth century, are being transformed before our eyes, with unprecedented speed."

"Not single theories and scientific hypotheses, these transient creations of reason, but precisely established new empirical correlations of exceptional value, force use to remodel and rebuild the picture of nature, which had remained intact and almost unchanged over several generations of thinkers" (Vernadskiy, 1934, p. 7).

V.I. Vernadskiy attached great importance to living organisms in all geochemical processes; he considered that living organisms form the most significant and inseparable part in the chemical discipline of the earth's crust. However, he considered the very approach of biologists to study of natural phenomena to be erroneous: "Biologists, studying living organisms, in the majority of their work, did not take the indissoluble connections existing between the environment and the living organisms into

^{*} Numbers in the margin indicate pagination in the foreign text.

consideration. Chearly recognizing the structure and function of an organism, they completely disregarded the discipline of the environment in which the organism lives, i.e. the biosphere. This environment was inert to them, independent of the organism, "cosmic." Thus, in studying an organism, they did not study the natural body, but the ideal product of their though" (p. 38), and further, "it is impossible to study and understand an organism, it is impossible to understand its shape and activity, not studying and not knowing the environment of life" (p. 39).

This concept of V. I. Vernadskiy was close to that toffthe Russian microbiologists S. N. Vinogradskiy, V. L. Omelyanskiy and B. L. Isachenko. The latter, beginning in 1914, was occupied with study of microorganisms in the oceans, seas, medicinal muds and other natural substances and, the last 10-15 years of his life, after organization of the Institute of Microbiology, he was dedicated to the geologic activities of microorganisms.

B. L. Isachenko was close to V. I. Vernadskiy, in the direction of his work. A characteristic trait of all his studies was, not only qualitative and quantitative recording of a natural phenomenon, but a precise identification of microorganisms participating in changes in the natural situation.

<u>/302</u>

Practically, he planned all the basic ways of study of the geochemical activity of microorganisms in oil and sulfur deposits, formation of calcite deposits and manganese concretions, and the like. After the death of B. L. Isachenko, his ideas became the foundation for further work of the Section on Geological Activity of Microorganisms, Institute of Microbiology, USSR Academy of Sciences, the contents of which are set forth in this report.

Microbiology of an Oil Stratum

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In study of the microflora of oil deposits, the question first arises as to the population of an oil stratum by microorganisms. There were two opinions: the microflora of stratal waters consists of relict forms and microorganisms generally are absentin the strata, and those found were brought into the stratum in the well drilling process. Colleagues of the Institute have carried out numerous analyses of the general population of microorganisms in stratal waters of various deposits, performed by the direct method and by inoculation on nutrient media.

It has been found in drilling out that water and petroleum from flowing wells of sealed deposits contain practically no microflora. Sealed deposits are sterile, and there are no relict microflora in them.

In water and petroleum from flowing wells of open deposits, with more or less water exchange in the stratum, microflora are found by microscopic recording or by growth on specific media, but there is no growth in beef extractmagar. This shows that the microflora penetrate into the deposit through an aquifer, and a specific biocenosis of microaerophils and anaerobes is created there. With prolonged exploitation of a stratum, the number of bacteria can increase to several million per ml of stratal water (Shturm, 1950a, b; Ekzertsev, 1951).

Finally, with artificial injection of water into a stratum, for the purpose of increasing the yield of petroleum from the stratum, or with production of petroleum by the compressor method, by means of injecting air, the population of bacteria increases sharply and, in individual cases, hydrocarbon-acidifying and nonsulfur purple bacteria appear (Isachenko, 1946; Rozanova, 1971). All this indicates transport of bacteria into the stratum from the surface of the earth and of reinforcing their reproduction by

3

creation of aerobic conditions in separate regions of the stratum. It is interesting to note that <u>Desulfovibrio salexigenes</u>, <u>Des.</u> <u>desulfuricans</u> var. aestuarii, <u>D. africanus</u> n. var. were discovered here.

Petroleum deposits, as a rule, atvthe same time, are enriched with natural gas, to a greater or lesser extent.

As the research of Barker and his colleagues showed (Barker, 1956), fatty acids, which are contained in small amounts in natural petroleums and stratal waters, are easily decomposed under anaerobic conditions, with formation of methane; moreover, formation of methane can proceed by reduction of carbon dioxide by molecular hydrogen, in the activities of Methanobacterium omelianskii.

The presence of these organisms has been detected in many petroleum deposits, and tests of anaerobic decomposition of petroleum have shown that, under laboratory conditions, the composition of the gases formed is close to that, which is dissolved in petroleum, and that which is extracted by deep samplers (Table 1) (Ekzertsev 1958).

The value of biogenic decomposition of petroleum, with formation of natural gas, in the opinion of KUB. Ashirov (1958), can be illustrated by the example of the Kalinovskiy petroleum deposit.

The formation of this deposit took place, owing to the fact that favorable conditions for accumulation of petroleum were created in the arch of the Kalinovskiy suite structural dome. Subsequently, in connection with the formation of favorable conditions for development of stratal microflora, the petroleum began to be subjected to decomposition to gaseous products. The gas formed began to squeeze the petroleum out to the southern

<u>/303</u>

TABLE 1. ANAEROBIC DECOMPOSITION OF PETROLEUM

Test conditions		Petroleum place of origin	Composition of gas formed, %			
			CH ₄	CO ₂	Н2	Н2
Test	Sterile petro- leum + bac- teria culture	mountäin,	21-24	2-2.9	0	75-76
		Pilyugina, Permian	34-35.4	2-4.3	0	61.4-62
		Novo-Stepa- novka, Permian	20-27	7.9-4.9	0	77.1-726
Gas from stratum	Withdrawn with deep sampler	Zol'ny ravine, Devonian	57-69	4.3-6.1	0	25.9-39.4
		Novo-Stepa- novka, Permian	48.4	0	0	51.6

limb, and the petroleum, receding, left a series of sealed residues, which were found by drilling at the present (Fig. 1), and our microbiological analyses have demonstrated a microflora population of the water-petroleum contact zone, which is destroying the petroleum, with formation of gas.

Sulfate Reduction

For more complete recovery of petroleum, the method of displacing it, by means of injection of water into the stratum through special force pumps, is being used more and more widely. Depending on the sulfate content of the injected water, or by contact of the petroleum collector with anhydrites by sulfate-enriched water, the sulfate reduction process arises in the petroleum stratum sooner or later. Thus, according to the data of M. V. Gasanov (1961), in the Ordzonikidze Petroleum deposit, into

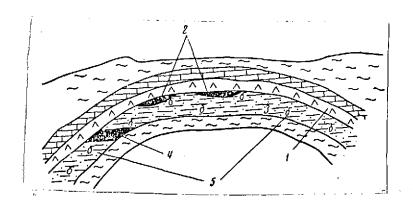


Fig. 1. Diagram of formation of natural gas deposits, owing to destruction of petroleum, using the example of the Kamenov-Novostepanov deposit (Ashirov, 1958): 1. anhydrite member; 2. petroleum remnants; 3. gas deposit; 4. petroleum saturation in steep limb; 5. bottom water.

which water from Lake Zabrat was injected initially and, subsequently, lake water mixed with water from the Caspian Sea, the appearance of hyrogen sulfide was detected 3 years after the start of flooding and, then, after formation of the corresponding bacterial complex of hydrocarbon-acidifying and sulfate-reducings bacteria, the process

of hydrogen sulfide formation intensified. Here, over a period of two months, the hydrogen sulfide content of the stratal water from some wells reached 500-600 mg/l. Formation of hydrogen sulfide was accompanied by corrosion of the deep well fittings.

/304

The rate of the sulfate reduction process was determined in a series of deposits, both by the increment of hydrogen sulfide in the stratum, on the basis of two analyses from the same well, and by the isotope method (Rozanova and colleagues, 1969; Ivanov, 1964; Ivanov, Gorlenko, 1966). As is evident from Table 2, these values amounted to 0.2-0.8 mg/l H_2S per day, and they depended to a considerable extent on the nature of the well operation.

Detailed studies of the mechanism of corrosion of the petroleum fittings were conducted in Baku in a number of fields, where injection of lake water into the same stratum was carried out (Rozanova and colleagues, 1969). The observations showed that particularly heavy corrosion is observed in the zone of contact of the lake water with the stratal water in wells approximately 600 m

TABLE 2. SULFATE REDUCTION RATE IN PETROLEUM STRATUM DURING ITS EXPLOITATION

	.†	: {		
Deposit	Water sample Characteristics	Number Number weof: wells	exploited	Average hydrogen sulfide formation rate, mg/l per day
Kasha-Naur	From stratum flooded with seawater	20		0.7
Pokrovskoye	From stratum flooded with with fresh water passing through anhydrite stratum	1	Seals, grade.	1.82
Shor-Su	From stratum pumped out with pumps, without flooding	. 22		0.17
Binagadninsk fold, Baku	From stratum into which salt water from Lake Beyuk-Shor is injected	<u> </u> 1		0.00
	Same	l	200	0.82
	4362Mes	1	600	0.30
	п	1	850	0.16
	From section of stratum not affected by injection			0.00

distant from the pressure zone (Table 2), when there still was almost no free hydrogen sulfide in the stratal water. Then, in proportion to the movement of the water along the stratum, the hydrogen sulfide concentration increases sharply, dissolved iron salts disappear from the stratal water and corrosion stops.

Detailed analyses of the sulfate-reducing bacteria population and the sulfate reduction rate showed that, when the water

approaches the petroleum boundary, sulfate reduction arises. Further, electrolytic corrosion arises in the petroleum fittings and the hydrogen formed is consumed by the sulfate reducing bacteria. The severest corrosion occurs in the hydrogen sulfate reduction process, when the hydrogen sulfide formed is bound to iron salts dissolved in the water. Finally, the iron is all bound to the hydrogen sulfide, sulfate reduction still takes place, becase of the organic matter of the petroleum, the amount of hydrogen sulfide increases sharply, it forms a protective film of iron sulfide onthe metal fittings, and the corrosion stops.

Detailed investigations of the petroleum and ozokerite layers of the Shor-Su and Borislavskiy folds (Rozanova, 1964) showed that bacteria are absent in the sealed petroleum lenses. Formation of ozokerite itself from petroleum takes place, by means of deposition of high-melting components in cracks from tectonic disruptions of the petroleum stratum isolation. Bacteria begin to work, when oxidation of the ozokerite to khorsane takes place. The aerobic, hydrocarbon-acidifying bacteria, Mycobacterium //305 mucosum, Brevibacterium maris and others, participate in this process. The field observations were confirmed by laboratory tests in percolators on ozokerite oxidation, with formation of a product of the khorsane type.

Role of Microorganisms in Formation and Destruction of Sulfurd Deposits

The participation of bacteria in the reduction of sulfates and formation of sulfur deposits was controversial 30 years ago. There were two points of view on this. A. S. Uklonskiy (1940) and a number of other geologists considered that the formation of hydrogen sulfide and its subsequent oxidation to sulfur proceeds abiogenically. Another point of view was held by B. I. Isachenko (1958). He considered that hydrogen sulfide is formed biogenically, and that its oxidation to sulfur takes place both chemically

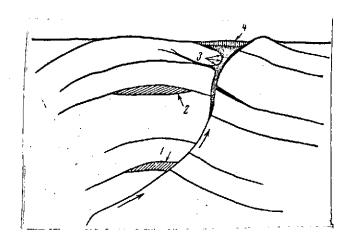


Fig. 2. Diagram of formation of ozokerite deposit (Rozanova, 1964): 1. petroleum stratum with disrupted isolation; 2. sealed petroleum dens, bacteria absent; 3. ozokerite; 4. khorsane enriched with hydrocarbon-acidifying bacteria.

and by means of the activities of thionic bacteria.

Taking the geological situation into consideration, observations in the field and of the physiology of thionic bacteria, he created a hypothesis of formation of sulfur deposits, in which an important role was discharged by microorganisms.

Later, on the basis of study of petroleum deposits,

it became clear that formation of hydrogen sulfide can occur exclusively biogenically (Ivanov, 1964), and that subsequent oxidation of sulfides to sulfur proceeds both chemically and by participation of <u>Thiobacillus thioparus</u>. Laboratory tests (Sokolova, Karavayko, 1962, 1964) demonstrated that this organism prefers microaerophilic conditions and grows well at $gH_2 = 17-21$. It can oxidize sulfur under neutral conditions and acidify the medium to pH 4.5, a value which is lethal for this organism.

The question as to whether or not oxidation of sulfur proceeds abiogenically, without participation of thionic bacteria, was controversial. Suitable tests (Sokolova, Karavayko, 1962), lasting 8 months (Fig. 3), showed that oxidation of sulfur takes places only in the presence of Th. thioxidans, in which the process begins, if the initial state of the nutrient medium is equal to or lower than pH 4.5, i.e. that value to which the nutrient medium is acidified by growth of Th. thioparus.

Thus, these organisms occupied two neighboring biological niches in nature.

The distribution of <u>Desulfovibrio</u>, <u>Th. thioparus</u> and <u>Th. thioparus</u> and <u>Th. thioparus</u> was studied in all the major deposits of the USSR: Shor-Su, Kara-Kum, Gaurdak, Rozdol'sk, Alekseyevsk, the volcanic sulfuredeposits in Kamchatka and many others. This made it possible to compare an adequately substantiated scheme of genesis of both epigenetic and syngenetic sulfur deposits.

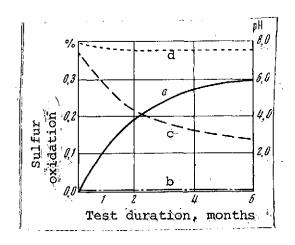


Fig. 3. Oxidation of native sulfur under laboratory conditions (Sokolova, Karavayko, 1962): a. 0xidation of sulfur in presence of Th. thiooxidans; b. same, under sterile conditions; c. change in pH in presence of Th. thiooxidans; d. same, under sterile conditions.

Epigenetic sulfur deposits include those, where sulfur was formed secondarily, in a sedimentary deposit which had already been formed. The mechanism itself of formation of such deposits is represented schematically in Fig. 4. (Ivanov, 1964). For formation of an epigenetic sulfur deposit, direct contact of the petroleum deposits with sedimentary rocks containing gypsum or anhydrite is necessary.

Saline stratal water of a petroleum deposit containing organic matter enters gypsum-containing rock through cracks or water-bearing horizons. The sulfate reduction process begins

here, with formation of hydrogen sulfide and deposition of secondary calcite.

In higher horizons, to which surface water bearing dissolved oxygen penetrates, the process of oxidation of hydrogenesulfide

/306

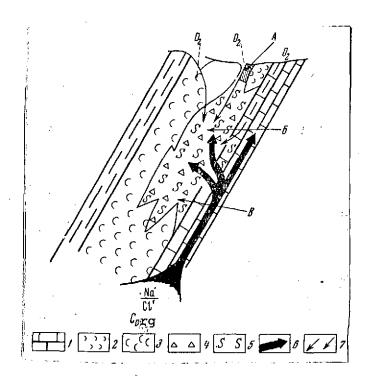


Fig. 4. Diagram of participation of microorganisms in formation and destruction of epigenetic sulfur deposit((Ivanov, 1964):
1. limestone; 2. gypsum; 3. anhydrite; 4. secondary calcite; 5. native sulfur segregation; 6. direction of movement of strongly mineralized water; 7. direction of movement of surface water, saturated with oxygen; A. Th. thiooxidans:

S + 1.502 + H2O + H2SO4; B. Th. thioparus: 2H2S + O2 + 2S + 2H2O and, simultaneously, chemical oxidation H2S + S; C. B. desulfuricans: CaSO4 + 2Corg + CaS + 2CO2; CaS + CO2 + H2O + H2S = CaCO3.

to molecular sulfur begins, chemically and with participation of Th. thioparus in approximately equal proportions. If the petroleum water head is high, the level of hydrogen sulfide water increases and protects the sulfur from further oxidation. Sulfur deposits are formed in this manner.

If the hydrogen sulfide water level begins to drop and the sulfur deposit finds itself on the surface, oxidation of it begins.

Initially, in alkaline strata and water, partial oxidation of the sulfur takes places with participation of Th. thioparus and, when the pH decreases to pH 4.5, Th. thiooxidans oxidizes the sulfur, acidifying the mine water to pH 0.5-1.0 as occurs in the

∰Gaurdak sulfur deposit (Ivanov, 1964).

The other type, syngenetic deposits, include those, in which sulfur formation occurs simultaneously with deposition of the intervening rocks.

The following can be pointed out as the most important conditions for formation of ore concentrations of elements, in the processoof formation of sedimentary sulfur deposits: 1) deposition rate of ore components; 2) effect of hydrodynamic regime of region; 3) dilution of deposited sulfur by terrigenous material (Strakhov, 1960).

The rate of deposition of sulfur is of exceptionally great importance in ore formation, which, in turn, depends on the rate of entry of hydrogen sulfide into the water, which either forms in bottom deposits or enters from outside. In the first case, in parallel with the formation of hydrogen sulfide in the sulfur reduction process, calcium carbonate forms.

$$CaSO_4 + 2C_{0EG} \rightarrow CaS + 2CO_2$$

 $CaS + H_2O + CO_2 \rightarrow CaCO_3 + H_2S$
 $2 H_2S + O_2 \rightarrow 2S^0 + 2 H_2O$

/307

Calculation of the products formed in this reactions shows that the CaCO₃/S ratio = 3.12, in other words, the sulfur content in the intervening rock should be 24.4%.

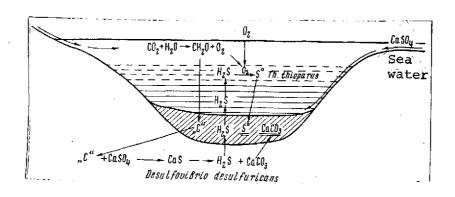


Fig. 5. Diagram of formation of syngenetic sulfur deposit in ocean lagoon.

If a large amount of terrigenous material is introduced into the reservoir from the water collecting area, the sulfur content in the deposits is insignificant. We have not succeeded in observing the modern process of syngenetic sulfur deposit formation, but all of the chief syngenetic deposits of the western Ukraine and middle Volga lands previously formed have been studied thoroughly. At the same time, lake-type reservoirs have been studied, in which the process of hydrogen sulfide formation is proceeding intensively in mud deposits. Considering the geological data and the results of microbiological analyses, a diagram can be compiled, showing the role of microorganisms in formation of syngenetic sulfur deposits (Fig. 5).

It can be assumed that syngenetic sulfur deposits were formed in fresh water reservoirs of the lagoon type, in the mud deposits of which an intensive sulfate reduction process took place. The hydrogen sulfide formation occurred with participation of sulfate- \(\frac{7308}{208} \) reducing bacteria. In maritime reservoirs, where there are excess sulfates, the principal regulating role is that of organic matter, the greatest production of which in maritime reservoirs is observed in shallow waters and well-heated lagoons; the most intensive photosynthesis took place here and, as a consequence of this, formation of hydrogen sulfide and a sulfur deposit took place (Fig. 5). If the introduction of terrigenous material was negligible, formation of syngenetic sulfur deposits occurred.

Role of Microorganisms in Formation of Manganese Deposits

The participation of microorganisms in the formation of iron-manganese deposits has been brought into question by geologists until recently (Strakhov and colleagues, 1968). The principal reason was that there was no success in finding an organisms participating in formation of sedimentary deposits of iron and manganese.

The first steps in this direction were taken by B. V. Perent fillyev (Berfillyev, 1952; Perfillyev, Gabe, 1961, 1964), using the capillary microscope method. An organism was found and called Metallogenium.

A whole series of difficulties arose in the path of obtaining a pure <u>Metallogenium</u> culture. There was no success in isolating <u>Metallogenium</u> from the mold accompanying it (Zavarzin, 1961, 1963).

The question was solved favorably, by use of a nutrient medium suitable for growth of Mycoplasmataceae, and the organism itself proved to be one of the Mycoplasma species, which was parasitic on molds and bacteria (Dubinina, 1969, 1970).

Its role in formation of manganese deposits was studied in detail in Lake Punnus-Yarvi, on the Karelian isthmus (Dubinina, Deryugina, 1967). Its distribution was studied in ores and the intervening rock of the Chiatur manganese deposit (Sokolova-Dubinina, Deryugina, 1966), and a comparison of the microbiological analyses with the geology of the adjacent regions made it possible to draw up a general concept of the role of microorganisms in the genesis of the deposits themselves.

Proceeding on the basis of the idea of N. M. Strakhov (1960), on the factors determining ore formation, we dwell on the following conditions: 1) hydrodynamic regime of the region from which manganese enters; the reservoir; 2) conditions favoring deposition of the ore-forming element, manganese in this case; 3) the conditions of its supplementary concentration in the diagenesis process; 4) the nature of the terrigenous dilutions.

Let us examine the role of microorganisms in all the processes stated above, which participate in formation of manganese deposits.

The first and chief circumstance is the entry of manganese into the reservoir. This problem is being solved by comparison of location of a manganese deposit or a lake, where manganese concretion formation is occurring, with the geological structure of the surrounding terrain. All lakes, in which contemporary accumulation of manganese is taking place, are located in the USSR and Scandinavian countries, on igneous rock of the Fenno-Scandian crystalline shield (Fedorova, 1964a, b; Rossolimo, 1964). Lake Baykal is bordered with igneous rock of the Khamar-Daban and Baykal ranges, and Lake Michigan is bordered by the Canadian crystalline shield. The Chiatur manganese depositsadjoins the Dzirul'sk granite massif, the rock of which contains up to 0.07% manganese, etc. Thus, the source of supply of manganese to reservoirs, in the form of solutions, colloids and suspensions is water from adjacent crystalline massifs. The process of weathering and erosion loss of manganese apparently takes place abiogenically.

Conditions favoring manganese deposition and supplementary concentration of it have been studied in detail in Lake Punnus-Yarvi (Sokolova-Dubinina, Deryugina, 1967), where active formation /309 of iron-manganese lake ores is occurring (Fig. 6).

Manganous oxides enter the lake from tributaries, in dissolved form, at concentrations of 0.1-1 mg/l. Its higher oxides are introduced predominantly from surface waters, in the form of suspensions and colloids. Manganese concentrations in the lake decrease to 0.01 mg/l, because of dilution of the inflows by lake water and their precipitation from solution. The manganous forms are oxidized in the water mass, by means of the activity of Metablogenium personatum. The manganic oxides formed, together with the suspensions and colloids, settle in mud deposits.

Concentration of the manganese salts takes place here in the mud deposits. In the diagenesis process, they are reduced, because

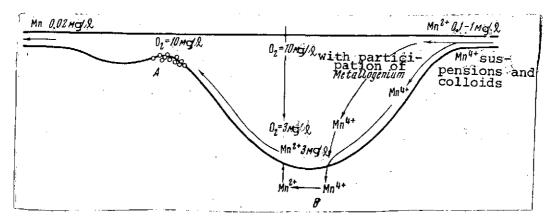


Fig. 6. Diagram of formation of iron-manganese lake ores (Sokolova-Dubinina, Deryugina, 1967):
A. in lake ore: Metallogenium, D. desulfuricans,
Bac. polymyxa, gH₂ = 18-37; B. in muds: Daedesul-furicans, Bac. circulans, Bac. polymyxa, gH₂ = 8-12.

of the activity of <u>Bac. circulans</u> and <u>Bac. polymyxa</u>. Following this, the manganous salts begin to diffuse into the water, and the Mn²⁺ concentrations in the native layers reaches 1.4-3 mg/L. The discharge of water from the lake and the constant outflow of dissolved manganous salts takes place through shallow water inlets, where sediments have a sufficiently high oxidation-reduction potential, which creates favorable conditions for the activity of Metallogenium.

Formation of iron-manganese concretions takes place with direct participation of <u>Metallogenium</u>, which is seen well in a comparison of microphotographs of <u>Metallogenium</u> growth in cultures with forms of its growth visible in thin microscopic sections of lake ore.

The ore formation process is absent in the deep section of the lake, into which all of the terrigenous material is removed, and it takes place actively in the shallow water, well-aerated part of the reservoir, where there is almost no accumulation of terrigenous material. Analyses have shown that practically all the manganese entering from tributaries is retained in the lake.

Of 14 tons of Mn brought in, only about 1 ton per year is removed from the lake (Stravinskaya and colleagues, 1971). Formation of iron and manganese ores in the Chiatur deposit apparently occurred in assimilar manner.

Geochemical Activity of Microorganisms in Nonferrous Metal Deposits

Mine waters in deposits of nonferrous metals frequently contain salts of copper, zinc, nickel and other metals in dissolved form. More than 300 years ago, this circumstance served as the basis, in the Rio Tinto mine in Spain, for artificial removal of copper in solution from tailings of spent ore, by means of sprinkling them with fresh water. There is no doubt at the present time that there is considerable participation by Th. ferro-oxidans in oxidation of nonferrous metal sulfides to sulfates.

How these bacteria are distributed in natural deposits and what their role is in the processes of oxidation of the ore body and infformation of secondary nonferrous metal sulfides has remained unclear. The results of field observations would be difficult to understand, without a detailed study of separate aspects of the physiology of the microorganisms carrying out the oxidation processes in deposits.

Thus, microbiological investigations were carried out on ores from deposits of copper, zinc, lead and cobalt, antimony, arsenic, rare earth elements, germanium and indium disseminated in galena and gold (Karavayko, 1970). The principal organisms and the sources of energy for their growth are presented schematically in Table 3.

These are <u>Th. ferrooxidans</u>, oxidizing the sulfides of a number of metals in an acid medium, <u>Th. "y"</u>, oxidizing the sulfides of metals under neutral conditions and a new organism, oxidizing the llower oxides of antimony to higher ones.

/310

TABLE 3. OXIDATION OF SULFIDES OF VARIOUS METALS (M)
BY THIONIC BACTERIA

Organism	General formula	<pre> Metal sulfides</pre>	Energy/ used	Authors
Th. ferrooxidans	$MS_2 \rightarrow MSO_4$	CuFeS ₂ ; Cu ₂ S, CuS		Brayner et al., 1954
p11 2—1	FeSO ₄ Fe ₂ (SO ₄) ₃	Cu _s FeS ₄ NiS; FeAsS: CoAsS	•	Lyalikova, 1961,
	$MS_2 + Fe_2 (SO_4)_3 \rightarrow MSO_4 + FeSO_4$			Lyalikova, Kuli- kova, 1969
Th. «y» pH 5—9	MS → MSO ₄	CuS; Cu ₂ S; Sb ₂ S ₃	*	Lyalikova: 1967
Th. n. sp.	$M_2O_y \rightarrow M_2O_b$	Sb₂O₃	$M^{+3} \rightarrow M^{+6}$	Lyalikova, 1972

The distribution of <u>Th. ferrooxidans</u> immonferrous metal deposits depends on three principal factors: the mineralogical composition of the ores, fracturing and flooding of the ore body. Of the copper-containing minerals, the ones most accessible to bacterial oxidation are covellite (CuS), chalcocite (Cu2S), chalcopyrite (CuFeS2), bornite (Cu5FeS4) and tetrahedrite (3Cu3S·Sb2S3).

The picture of the dependence of oxidative processes on ore composition, fracturing and flooding can be seen particularly clearly on the walls of the open pit of the copper mine in Kounrade.

It is well-known that all biological processes depend to the greatest extent on the temperature of the environment. However, geological data show that sulfide copper and nickel deposits, located on the Koła peninsula, even above the Arctic@Circle, are covered with an "iron hat," consisting of ferric oxide ores.

In connection with this, distribution of <u>Th. ferrooxidans</u> above the Arctic Circle has been studied in old mine shafts, where

the natural processes of oxidation of residual ores took place after the main deposit was worked out, in a period of 10-15 years, at low ambient temperatures. Th. ferrooxidans was discovered simultaneously in acid waters passing through the ore body and having temperatures of about 4° and in drips from the walls of drifts in strata being exploited.

Tests to determine its growth rate (Karavayko, Moshnyakova, 1971) were carried out by the isotope method, and they showed that the generation time of the bacteria at a temperature of 6° , observed in a mine shaft, was 3 days, while, in this same water, incubated at 20° , it was not over 12-24 hours. In other words, direct tests show that the processes of oxidation of copper and nickel sulfides takes place at the low temperatures of an ore stratum above the Arctic Circle.

As has malready been pointed out, the geochemical activity of microorganisms is greatly inhibited, because of a deficit of moisture. In connection with this, we examined a series of deposits in the arid regions of Kazakhstan. Actually, slight bacterial activity was observed in the Dzhezkazgan deposits, but the ores in them were distinguished by low oxidation states.

However, a large number of ores arecencountered here, which are secondary copper sulfides.

The Dzhezkazgan deposit attracted attention by the extensive distribution of sulfate-reducing bacteria, which are capable of using organic matter scattered in the rock for their growth in build-up cultures (Lyalikova, Sokolova, 1965).

The wide distribution of <u>Desulfovibrio desulfuricans</u> in deposits, their capability of reducing sulfates using the organic matter of the intervening rock and of growing in copper concentrations of up to 50 mg/l, as well as its presence in the form of

/311

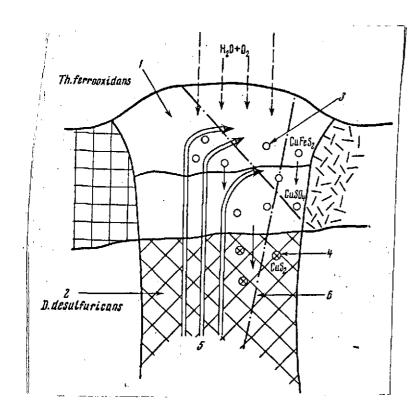


Fig. 7. Diagram of secondary copper sulfide formation: 1. oxidation zone; 2. hydrogen sulfide formation zone; 3. primary copper sulfides; 4. secondary copper sulfides; 5. ore-bearing fluids; 6. direction of tectonic fractures.

secondary sulfides in ore deposits, all indicate that secondary sulfides also are products of the geological activity of microorganisms.

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As a result of intrusions, deep rocks and waters reach the surface. Orecarrying solutions deposit primary coppera and iron sulfides, forming an ore body. As a result of tectonic disruptions, fractures form in the ore body; if surface water trickles through them, the oxidation process begins.

sulfides are oxidized to limonites, forming an "iron hat" above the deposit. Copper sulfides are oxidized to copper sulfates and, being more mobile, they go down to deeper horizons through the fractures, in the region of activity of sulfate-reducing bacteria. Reacting with hydrogen sulfide, the copper sulfates form secondary sulfides (Fig. 7). By the example of the Koundar and Dzhezkazgan copperadeposits, this is the geochemical activity of microorganisms in nonferrous metal deposits.

<u>/312</u>

Such are the results of theoretical investigations of the geochemical activity of microorganisms in mineral deposits.

Among the practical measures which flow from development of the

theory of geochemical processes are microbiological methods of prospecting for petroleum and gas deposits (Mogilevskiy, 1957), control of petroleum equipment corrosion (Kuznetsova, 1964; Rozanova and colleagues, 1969), the preservation of stored copper ores (Karavayko, 1969), cleansing impurities from ore concentrates (Pol'kin and colleagues, 1969), underground and mound leachingout of nonferrous metals from spent ores (Golomzik and colleagues, 1967), microbiological methods of extraction of disseminated rare earth metals and gold from sulfide ores, with destruction of the crystal lattices of the primary mineral (Lyalikova, 1970; Lyalikova, Mokeycheva, 1969). With the example of study of the geological activity of microorganisms, the words of Pasteur, which he spoke in 1871, i.e. 100 years ago, are vindicated: "There is no, a thousand times there is no category of science, which could be called applied science. There is science and application of science. They are interconnected, like the fruit and the tree to which they belong" (Pasteur, 1960).

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